

UNCLASSIFIED

Defense Technical Information Center  
Compilation Part Notice

ADP012377

TITLE: Mechanism and Kinetics of Iodine Dissociation in COIL

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Gas and Chemical Lasers and Intense Beam Applications III Held  
in San Jose, CA, USA on 22-24 January 2002

To order the complete compilation report, use: ADA403173

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:

ADP012376 thru ADP012405

UNCLASSIFIED

# Mechanism and kinetics of iodine dissociation in COIL

Michael C. Heaven\*, Anatoly V. Komissarov and Vasilij Goncharov,  
Department of Chemistry, Emory University, Atlanta, GA 30322

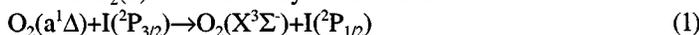
## ABSTRACT

Dissociation of  $I_2$  by  $O_2(a^1\Delta)$ , with subsequent excitation of  $I^*$ , was first observed by Arnold *et al.*<sup>1</sup> in 1966. This key discovery led to the eventual development of the chemical oxygen iodine laser (COIL). The mechanism by which  $I_2$  is dissociated was not determined by Arnold *et al.*<sup>1</sup> and has remained elusive, despite many experimental attempts to unravel this question. Although the details are not known, it is apparent that a complex interplay between vibrationally and electronically excited states of  $I_2$  is involved. Vibrationally excited states of  $O_2$  have also been implicated. Characterization of the dissociation process is an important issue for COIL as the efficiency is impacted by the energy cost of dissociating the iodine. In this paper we provide a historical summary of work on the dissociation mechanism, and summarize the current understanding of the problem.

Keywords: Chemical lasers, oxygen, iodine, reaction kinetics, energy transfer.

## 1. INTRODUCTION

In 1966 Arnold *et al.*<sup>1</sup> reported the key observations that led to the eventual development of the chemical oxygen iodine laser (COIL). They found that adding  $I_2$  to a flow of excited oxygen produced emissions from  $I_2(B^3\Pi(O_u^+))$ ,  $I(^2P_{1/2})$  (denoted as  $I^*$  in the following), and  $O_2(b^1\Sigma^+)$ . The reactions responsible for excitation of  $I^*$  and  $O_2(b)$  were correctly identified as



and



However, Arnold *et al.*<sup>1</sup> were unable to resolve the question of how  $I_2$  was initially dissociated. The energy levels of  $O_2$ ,  $I_2$  and  $I$  that are relevant to this problem are shown in Fig. 1. As  $O_2(a)$  does not carry enough energy to dissociate  $I_2$  in a single collision, Arnold *et al.*<sup>1</sup> speculated that the first encounter could populate an excited state of  $I_2$ , and a second  $O_2(a)$  molecule would dissociate this excited species. This can be represented by the sequence



An alternative explanation is that  $O_2(b)$  directly dissociates  $I_2$ . Arnold *et al.*<sup>1</sup> demonstrated that  $O_2(b)$  could be generated in a flow of  $O_2(a)$  by the pooling reaction



The dissociation mechanism is a matter of importance for COIL as this process consumes an appreciable amount of energy. In a flow tube study, Alsing *et al.*<sup>2</sup> found that approximately six  $O_2(a)$  molecules were needed to dissociate one  $I_2$  molecule under optimized conditions. For less favorable reagent ratios up to sixteen  $O_2(a)$  molecules were needed to dissociate one  $I_2$ . In addition to consuming energy, the kinetics of the dissociation process can also influence the power extraction efficiency in a laser system. The time scale for dissociation determines the downstream position at which the maximum concentration of  $I^*$  will occur. If dissociation takes place too slowly the maximum  $I^*$  concentration will be achieved after the gas has left the optical cavity. Conversely, if high concentrations of  $I^*$  are formed before reaching the optical cavity, energy is lost during transport (mostly due to quenching by  $H_2O$  from the  $O_2(a)$  generator). This leads to a curious situation where the conditions that give maximum power from the laser do not correspond to complete dissociation of  $I_2$ .<sup>3,4</sup>

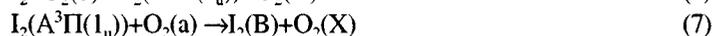
Since the seminal work of Arnold *et al.*<sup>1</sup> there have been several attempts to unravel the details of the dissociation mechanism. A generally accepted model was established in 1988, and optimal values for the most important rate constants were proposed<sup>5,6</sup>. The model was developed using data from kinetic studies of elementary reactions and analyses of device performance characteristics. It has been used for most

\* [heaven@euch4e.chem.emory.edu](mailto:heaven@euch4e.chem.emory.edu). Phone (404) 727 6617, FAX (404) 727 6586

subsequent computational studies of COIL systems. Due to the method of construction, the model does a good job of reproducing the behavior of well-characterized devices. However, it cannot be relied upon to predict the properties of devices running under non-standard conditions (e.g., high pressures and/or novel gas mixing geometries). Consequently, computational predictions for untested conditions or new hardware cannot be trusted. As we will discuss in this article, the problems stem from the fact that we still do not have a complete understanding of the dissociation process.

## 2. THE FIRST QUANTITATIVE MODEL: DISSOCIATION OF I<sub>2</sub> BY O<sub>2</sub>(b)

Derwent and Thrush<sup>7-10</sup> used flow tube techniques to examine the oxygen-iodine system. The kinetics were followed by monitoring emissions from I<sub>2</sub>(B) and I\*. Arnold *et al.*<sup>1</sup> had assumed that I<sub>2</sub>(B) was formed by I\*+I+M recombination, but Derwent and Thrush<sup>7</sup> were able to show that it is produced by sequential excitation of I<sub>2</sub>. They proposed the mechanism



but did not consider the excited states of I<sub>2</sub> to be important in the dissociation process. Their analysis of the kinetics led to the conclusion that I<sub>2</sub> was dissociated by<sup>8</sup>



This reaction set, along with the pooling reactions 2 and 5, provided a satisfactory representation of the observed emission signals. Derwent and Thrush<sup>10</sup> also used the equilibrium between reaction 1 and the reverse process



to evaluate the radiative lifetime of I\*. In considering these data they realized that reaction 1 could sustain CW lasing on the I\*→I transition. The subsequent demonstration of a chemically driven O<sub>2</sub>(a)/I\* laser<sup>11,12</sup> (as described in the preceding paper by McDermott<sup>13</sup>) stimulated further studies of O<sub>2</sub>/I<sub>2</sub> kinetics.

## 3. THE CHAIN DISSOCIATION MECHANISM AND PROBLEMS WITH THE IDENTITY OF I<sub>2</sub><sup>†</sup>.

The model proposed by Derwent and Thrush<sup>7,8</sup> required a gas kinetic rate constant (~2x10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup>) for the removal of O<sub>2</sub>(b) by I<sub>2</sub>. Using pulsed laser excitation of O<sub>2</sub>(b,v=0), Houston and co-workers<sup>14,15</sup> made direct measurements of the removal rate constant. The value they obtained, 2x10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup>, was too small to account for the flow tube results. Consequently, Heidner *et al.*<sup>16</sup> performed a careful and systematic reinvestigation of the I<sub>2</sub>/O<sub>2</sub>(a) kinetics. Fluorescence signals from I<sub>2</sub>(B), I<sub>2</sub>(A), I\*, O<sub>2</sub>(b) and O<sub>2</sub>(a) were monitored in flowing I<sub>2</sub>/O<sub>2</sub>(a) mixtures. The dependence of the I<sub>2</sub> dissociation rate on the presence of H<sub>2</sub>O was also examined; the motivation being that H<sub>2</sub>O was present in the flow from chemical O<sub>2</sub>(a) generators, and it was expected to have a deleterious effect on the dissociation rate. Heidner *et al.*<sup>16</sup> established the most important characteristics of the dissociation process. They found that there was a slow initiation step followed by rapid, branched-chain dissociation of I<sub>2</sub>. I\* was identified as the chain carrier. Noting that the dissociation rate was dependent on the initial concentration of I<sub>2</sub>, they also suggested that an excited state of I<sub>2</sub> was the precursor to atomic iodine. The reaction scheme used to model these observations was as follows. The slow initiation step was attributed to reaction 3. This was followed by the rapid dissociation of I<sub>2</sub><sup>†</sup> by reaction 4. I atoms liberated by this sequence are excited by reaction 1, permitting I\* to carry the chain via the reaction



As expected, the presence of H<sub>2</sub>O did slow the dissociation rate. It was known that both O<sub>2</sub>(b) and I\* were effectively quenched by H<sub>2</sub>O, but when Heidner *et al.*<sup>16</sup> modeled their results they found that these were not the primary reactions influencing the dissociation rate. Instead, the models required gas kinetic (2x10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup>) deactivation of I<sub>2</sub><sup>†</sup> by H<sub>2</sub>O



Heidner *et al.*<sup>16</sup> attempted to define a sub-set of critical rate constants by fitting to their dissociation rate data. Unfortunately, several of the rate constants could not be uniquely determined as they were strongly

correlated. Two limiting rate constant sets were offered as constraints on a yet-to-be-determined set of final values. Three of the rate constants differed by more than an order of magnitude between the two models. Heidner *et al.*<sup>16</sup> also noted that their models were not completely satisfactory, as they could not find a single set of parameters that could represent all of the data. They did find that the original Derwent and Thrush<sup>8</sup> model gave acceptable results, but concluded that "the agreement with experiment is moderately good, but, based on the direct measurements of Houston and co-workers, such agreement must be fortuitous".

Hediner *et al.*<sup>16</sup> discussed possible assignments for  $I_2^\dagger$ . Within the framework of their model there were two plausible alternatives. Either  $I_2^\dagger$  was vibrationally excited  $I_2(X)$  or the metastable electronically excited species  $I_2(A'^3\Pi(2_u))$ . There were troubling difficulties with both of these choices.  $I_2(A')$  has an excitation energy of 10,042  $\text{cm}^{-1}$ , so it cannot be accessed by energy transfer from  $O_2(a)$  ( $T_0=7882 \text{ cm}^{-1}$ ). Near-resonant transfer from  $O_2(a)$  or  $I^*$  would populate  $I_2(X)$  vibrational levels in the range of  $v=40-50$ . Experiments performed by Hall *et al.*<sup>17</sup> showed that  $I^*$  was rapidly quenched by  $I_2$  ( $k=3.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ), and that vibrationally excited  $I_2(X)$  was formed in the process. Van Bentham and Davis<sup>18</sup> later went on to show that vibrationally excited  $I_2(X)$  was generated when  $I_2$  was added to a flow of  $O_2(a)$ . The problem, with regard to assigning  $I_2^\dagger$  to vibrationally excited  $I_2(X)$ , was that Hall *et al.*<sup>17</sup> reported rapid relaxation of  $I_2(X, v=40)$  by Ar. This result appeared to be at variance with Heidner *et al.*'s<sup>16</sup> observation that the dissociation rate was not influenced by the presence of Ar. This conflict could be resolved by recognizing that several vibrational energy transfer collisions would be needed to relax the initially formed  $I_2(X, v=40)$  to levels that did not have sufficient energy to be dissociated by a collision with  $O_2(a)$  ( $I_2(X, v < 20)$ ). Assuming that the vibrational relaxation rate constant measured by Hall *et al.*<sup>17</sup> corresponded to  $\Delta v = -1$  transfer, David *et al.*<sup>19</sup> used kinetic modeling to show that the vibrational cascade process would not be fast enough to impact the dissociation rate for the conditions of Heidner *et al.*'s<sup>16</sup> experiments. With this insight it was concluded that  $I_2^\dagger$  is the vibrationally excited species, and Heidner *et al.*'s<sup>16</sup> model 1 rate constants were adopted for subsequent simulations of COIL devices. However, lingering doubts concerning the identity of  $I_2^\dagger$  remained. Lilenfeld<sup>20</sup> compared the effects of  $H_2O$ ,  $CO_2$ , and  $SF_6$  on the dissociation rate. He found that  $H_2O$  and  $CO_2$  were very effective in deactivating  $I_2^\dagger$ , while  $SF_6$  was about 8 times less effective than  $CO_2$ . It was surprising to find that  $SF_6$  was not the best deactivator, as this molecule has many vibrational modes that can accept vibrational energy from  $I_2$ . Based on these observations Lilenfeld<sup>20</sup> favored the notion that  $I_2^\dagger$  is the electronically excited species  $I_2(A')$ . He noted that  $O_2(a, v=1)$  has almost enough energy to excite  $I_2(A')$ , and used EPR spectroscopy to show that  $O_2(a, v=1)$  was present in the flow from his singlet oxygen generator.

Several excited states of  $I_2$  could be involved in the process where  $O_2(a)$  dissociates  $I_2(A')$ . Emission from  $I_2(B)$  is seen in  $O_2(a)/I_2$  flames, and it had been suggested that reaction 7 and  $I_2(A') + O_2(a) \rightarrow I_2(B) + O_2(X)$ , followed by predissociation of  $I_2(B)$  were the source of I atoms. Lilenfeld<sup>20</sup> was able to eliminate these channels by demonstrating that strong magnetic fields, which accelerate the  $I_2(B)$  predissociation rate, do not increase the overall dissociation rate.

#### 4. IS $I_2^\dagger$ VIBRATIONALLY EXCITED $I_2(X)$ ? A CLOSER LOOK.

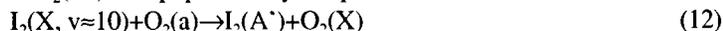
Lilenfeld<sup>20</sup> and Heidner *et al.*<sup>16</sup> had drawn attention to the puzzling characteristics of  $I_2^\dagger$  deactivation. This species was rapidly removed by  $H_2O$  and  $CO_2$ , while collisions with He or Ar were less effective by orders of magnitude. For example, in Heidner *et al.*'s<sup>16</sup> model 1 the rate constants for deactivation of  $I_2^\dagger$  are (in units of  $\text{cm}^3 \text{ s}^{-1}$ )  $3 \times 10^{-10}$  ( $H_2O$ ),  $5 \times 10^{-11}$  ( $O_2(X)$ ), and  $4 \times 10^{-12}$  (Ar). These trends are more typical of electronic quenching, rather than vibrational relaxation. Heaven and co-workers<sup>21-24</sup> examined the viability of equating  $I_2^\dagger$  deactivation with  $I_2(X)$  vibrational energy transfer by studying the relaxation process under well-controlled conditions. Individual ro-vibrational levels of  $I_2(X)$  in the range  $22 < v < 43$  were populated using a pulsed stimulated emission pumping technique. The excited molecules were allowed to make a few collisions with the surrounding bath gas, and then the pulses from a probe laser were used to observe the range of levels populated by energy transfer. Fig. 2 shows results from this type of measurement. In this instance  $I_2(X)$  was excited to the  $v=23, J=57$  level (where J is the rotational quantum number). The upper panel in Fig. 2 shows a probe laser spectrum taken under collision free conditions. The  $J=57$  population gives rise to just two spectral lines that obey the  $\Delta J = \pm 1$  selection rule. The lower panels show the results of colliding  $I_2(v=23, J=57)$  with Ar and  $H_2O$ . Most of the lines in these traces originate from rotationally inelastic collisions

( $\Delta v=0$  transfer). The lines marked with asterisks are the result of  $v=23 \rightarrow 22$  transfer. From these traces it can be seen that the probabilities for vibrational relaxation by  $\text{H}_2\text{O}$  and Ar are comparable. Modeling of these data indicates that vibrational relaxation by  $\text{H}_2\text{O}$  is about a factor of two faster than relaxation by  $\text{Ar}^{24}$ . The rate constants do not differ by a factor of 75, as required by the models of  $\text{I}_2^\dagger$  deactivation. The absolute magnitudes of the vibrational relaxation rate constants also pose a problem. For relaxation by  $\text{H}_2\text{O}$  the total removal rate constant was  $1.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , and this was dominated by  $\Delta v=-1$  transfer. This is only half of the  $\text{I}_2^\dagger$  deactivation rate constant, without considering the damping effect of the vibrational cascade sequence. Models of  $v=40 \rightarrow 20$  relaxation<sup>24</sup> predict an overall deactivation rate constant for  $\text{H}_2\text{O}$  of  $8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ .

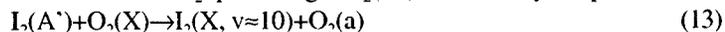
Although the vibrational relaxation rate constants were in gross disagreement with the limiting deactivation rate constants of Heidner *et al.*<sup>16</sup>, this did not mean that the identification of  $\text{I}_2^\dagger$  as  $\text{I}_2(\text{X}, v>20)$  had necessarily been invalidated. Heidner *et al.*<sup>16</sup> stated that their rate constant set was not unique. Consequently, Paschkewitz and Heaven<sup>25</sup> explored the possibility of re-optimizing the rate constant package with the  $\text{I}_2^\dagger$  deactivation rate constants constrained to values that were compatible with the vibrational relaxation rate constant measurements. The model was fit to Heidner *et al.*'s<sup>16</sup> dissociation rate data. It was found that the value of the  $\text{H}_2\text{O}$  deactivation rate constant could be reduced to a minimum value of  $4.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , but this was still too large to be consistent with vibrational relaxation. Other problems with the re-optimized model were that it could not tolerate deactivation by Ar and the dissociation rates predicted for low concentrations of  $\text{H}_2\text{O}$  were in poor agreement with the experimental data<sup>25</sup>. The conclusion drawn from these efforts was that  $\text{I}_2(\text{X}, v>20)$  is not the immediate precursor of atomic iodine. Although  $\text{I}_2(\text{X}, v>20)$  may play an important role in the dissociation mechanism, the deactivation kinetics are governed by a different species.

## 5. IS $\text{I}_2^\dagger$ ELECTRONICALLY EXCITED $\text{I}_2$ ?

Emission from  $\text{I}_2(\text{A}^3\Pi(1_0))$ ,  $\tau_{rad}=220 \mu\text{s}$  is readily observed from  $\text{O}_2(\text{a})/\text{I}_2$  flames<sup>16,26</sup>, but the lowest energy electronically excited state of  $\text{I}_2$  ( $\text{A}^3\Pi(2_0)$ ) is very metastable, and cannot be detected by emission spectroscopy. Basics *et al.*<sup>27</sup> used laser excitation techniques to demonstrate that  $\text{I}_2(\text{A}')$  was generated in  $\text{O}_2(\text{a})/\text{I}_2$  mixtures. They found that  $\text{I}_2(\text{A}')$  and  $\text{I}_2(\text{X}, v>20)$  were present at comparable concentration levels. Barnault *et al.*<sup>28</sup> proposed that  $\text{I}_2(\text{A}')$  was populated by the process



Support for this mechanism was provided by a study of the  $\text{I}_2(\text{X})$  vibrational population distribution in a flowing  $\text{I}_2/\text{O}_2(\text{a})$  mixture. Barnault *et al.*<sup>28</sup> observed selective depletion of vibrational levels around  $v \approx 10$ , indicating that this population was being removed by reaction 12. The dissociation mechanism proposed by Barnault *et al.*<sup>28</sup> was dependent upon vibrational excitation of  $\text{I}_2(\text{X})$ , but the kinetics were controlled by passage through the  $\text{A}'$  state. Additional kinetic schemes involving  $\text{I}_2(\text{A}')$  were elaborated by Bouvier *et al.*<sup>29</sup> These models could accommodate the fact that moderate pressures of Ar or He had very little influence on the dissociation rate. Tellinghuisen and Phillips<sup>30</sup> had reported rate constants for removal of  $\text{I}_2(\text{A}')$  by He and Ar of  $0.94 \times 10^{-14}$  and  $2.8 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ , respectively. The small rate constants were consistent with removal via collision induced dissociation. Quenching of  $\text{I}_2(\text{A}')$  by molecular collision partners that could accept energy by E-E or E-V transfer was expected to be much more effective. Tellinghuisen and Phillips<sup>30</sup> observed a self-quenching rate constant of  $5.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . These trends provided some indication that  $\text{I}_2(\text{A}')$  could be the key intermediate, but data for the quenching of  $\text{I}_2(\text{A}')$  by  $\text{H}_2\text{O}$  and  $\text{O}_2(\text{X})$  were needed to further explore this possibility. Komissarov *et al.*<sup>31</sup> measured these rate constants using pulsed laser pump-probe techniques. Quenching rate constants of  $6.3 \times 10^{-12}$  and  $3.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  were obtained for  $\text{O}_2(\text{X})$  and  $\text{H}_2\text{O}$ , respectively. Clearly, these collision partners were much more effective quenchers than He or Ar, but the quenching still appeared to be slower than that required for  $\text{I}_2^\dagger$  deactivation. Furthermore,  $\text{O}_2$  was more effective in removing  $\text{I}_2(\text{A}')$  than  $\text{H}_2\text{O}$ , in conflict with the ordering of the deactivation rate constants. Komissarov *et al.*<sup>31</sup> suggested that the latter problem could be resolved if  $\text{O}_2$  quenching of  $\text{I}_2(\text{A}')$  occurred by the process



which would minimize the loss of energy and permit facile re-excitation. Conversely, it was assumed that quenching by  $\text{H}_2\text{O}$  caused irreversible deactivation to the lowest vibrational levels of  $\text{I}_2(\text{X})$ . The remaining problem was the low absolute magnitudes of the  $\text{I}_2(\text{A}')$  quenching rate constants. This could be

accommodated in the model by reducing the rate constants for excitation and dissociation of  $I_2(A')$ , thereby allowing the deactivation processes to compete. The resulting kinetic scheme is illustrated in Fig. 3.

An attempt to derive rate constants for the revised kinetics package was made by modeling the data of Heidner *et al.*<sup>16</sup> The performance of the revised model was comparable to that of Heidner *et al.*'s<sup>16</sup> limiting case models. Once again it was found that the available data were not sufficient to define a unique set of rate constants. Komissarov *et al.*<sup>31</sup> concluded that their model was capable of reproducing the dissociation rate data, and presented one set of physically reasonable rate constants as an example. Subsequently, Bruins *et al.*<sup>32</sup> and Madden<sup>33</sup> have modeled the performance of COIL devices using the Komissarov *et al.*<sup>31</sup> rate constants. They found poor agreement with the experimental data, primarily due to underestimation of the  $I_2$  dissociation rate. This failure shows that the rate constant package contains errors, it does not necessarily imply that the mechanism is incorrect. The model has sufficient flexibility that fitting the rate constants to flow tube and COIL performance data would provide a parameterized model that would work as well as the standard model. However, this would be an exercise of questionable value, as it cannot be used to distinguish the true mechanism from functionally equivalent models. Further studies of the elementary reactions are needed to assess the viability of the mechanism proposed by Komissarov *et al.*<sup>31</sup>

## 6. IS VIBRATIONALLY EXCITED $O_2$ IMPORTANT IN THE DISSOCIATION PROCESS?

The crux of the problem with models that are dominated by the kinetics of an  $I_2^\dagger$  intermediate is the relative ordering of the deactivation rate constants,  $k_{H_2O}^\dagger \approx 6k_{O_2}^\dagger > 75k_{Ar}^\dagger$ . The Derwent and Thrush<sup>7,8</sup> model was successful because  $H_2O$  is the most efficient quencher of  $O_2(b)$ . Houston and co-workers had shown that dissociation by  $O_2(b, v=0)$  was untenably slow, but alternative mechanisms involving vibrationally excited  $O_2(b)$  and  $O_2(a)$  have been advanced. As noted above, Lilenfeld<sup>20</sup> detected  $O_2(a, v=1)$  in his experiments, and suggested that  $I_2(A')$  could be directly excited by this species. More recently, Azyazov *et al.*<sup>34</sup> observed  $O_2(a, v=1)$  in the flow from a jet-type singlet oxygen generator. In these experiments the evidence for the presence of  $O_2(a, v=1)$  was provided by detection of the  $O_2(a, v=1)-O_2(a) \rightarrow O_2(X)-O_2(X)$  dimole emission band. Azyazov *et al.*<sup>34</sup> estimated that about 2% of the  $O_2(a)$  in their system was vibrationally excited. They suggested possible roles for vibrationally excited  $O_2$  in the dissociation mechanism that included  $O_2(a, v>0)+I_2(X) \rightarrow O_2(X) + I_2(A')$ , and gas kinetic dissociation of  $I_2(X)$  by  $O_2(b, v>0)$ . Processes that might generate vibrationally excited  $O_2$  include



Models based on these reactions will no doubt be able to reproduce the flow tube and laser performance data, once the rate constants have been empirically adjusted. As with the previous models, it will not be possible to evaluate the reality of the model as the required rate constants and final state distribution data are not available. Measurements of a few key rate constants should be undertaken to assess the importance of these reactions.

## 7. CONCLUSION

Thirty six years ago Arnold *et al.*<sup>1</sup> noted that "A more difficult question is how the  $I_2$  is initially dissociated". Their comment remains valid. Important details of the dissociation mechanism have been gleaned from careful kinetic measurements, but this data set is still far from complete. Models of the dissociation process have been further elaborated and refined by fitting to laser performance characteristics. Unfortunately, the complexity of the process does not allow the mechanism to be determined by this approach. Since the establishment of the standard reaction set and rate constant package used to model COIL devices, investigations of specific reactions have shown that some of the critical rate constants are incorrect, and have called the accepted mechanism into question. At this point the standard model should be regarded as an intelligent parameterization, rather than a correct physical description.

The majority of the data used to establish the COIL kinetics package was recorded more than fifteen years ago. The generation of researchers who revealed the potential of the  $I_2/O_2(a)$  system, and mapped the functional characteristics of the  $I_2$  dissociation process, did so through elegant application of a limited set of diagnostic tools. Since that time advanced techniques for characterizing the key species in COIL systems have been developed, as described in the paper by Davis<sup>35</sup>. Application of the full range of diagnostic techniques in new studies of the dissociation mechanism will lead to a final resolution of this long-standing problem. The development of truly predictive computational models for COIL devices will then be in reach.

## ACKNOWLEDGMENT

Support provided by the Air Force Office of Scientific Research for work on the reaction kinetics of the  $I_2/O_2(a)$  system led to the demonstration of the first COIL system. AFOSR has sustained its commitment to fundamental studies of reaction dynamics, which is reflected in the fact that the greater majority of the research described in this article was sponsored by AFOSR. The authors are grateful for the continued support of these efforts at Emory University through AFOSR grant F49620-01-1-0070.

## REFERENCES

1. S. J. Arnold, N. Finlayson, and E. A. Ogryzlo, "Some novel energy-pooling processes involving  $O_2(a)$ " *J. Chem. Phys.* **44**, 2529 (1966).
2. P. M. Alsing, S. J. Davis, and G. L. Simmons. "Efficiency of the dissociation of  $I_2$  by  $O_2(a)$ " unpublished preprint.
3. B. D. Barmashenko and S. Rosenwaks, "Power dependence of chemical oxygen-iodine lasers on iodine dissociation," *AIAA J.* **34**, 2569-2574 (1996).
4. C. A. Helms, J. Shaw, G. D. Hager, "Iodine dissociation in COILs," *Proc. SPIE-Int. Soc. Opt. Eng.* **2502**, 250-7 (1995).
5. G. P. Perram and G. D. Hager, "Standard chemical oxygen-iodine laser kinetics package" Air Force Weapons Lab., Kirkland AFB, NM. 1988.
6. G. P. Perram and G. D. Hager, "Standard chemical oxygen-iodine laser kinetics package, Revision" Air Force Weapons Lab., Kirkland AFB, NM. 1988.
7. R. G. Derwent and B. A. Thrush, "Excitation of iodine by singlet molecular oxygen. 1. Mechanism of the iodine chemiluminescence," *J. Chem. Soc., Faraday Trans. 2* **68**, 720-8 (1972).
8. R. G. Derwent and B. A. Thrush, "Excitation of iodine by singlet molecular oxygen. 2. Kinetics of the excitation of the iodine atoms," *Faraday Discuss. Chem. Soc. No.* **53**, 162-7 (1972).
9. R. G. Derwent, David R. Kearns, and Brian A. Thrush. "Excitation of iodine by singlet molecular oxygen," *Chem. Phys. Lett.* **6**, 115-16 (1970).
10. R. G. Derwent and B. A. Thrush, "Radiative lifetime of the metastable iodine atom  $I(5^2P_{1/2})$ ," *Chem. Phys. Lett.* **9**, 591-2 (1971).
11. D. J. Benard, W. E. McDermott, N. R. Pchelkin, and R. R. Bousek, "Efficient operation of a 100 W transverse-flow oxygen-iodine chemical laser," *Appl. Phys. Lett.* **34**, 40-1 (1979).
12. W. E. McDermott, N. R. Pchelkin, D. J. Benard and R. R. Bousek, "An electronic transition chemical laser," *Appl. Phys. Lett.* **32**, 469-70 (1978).
13. W. E. McDermott, "Historical Perspective of COIL," *Proc. SPIE-Int. Soc. Opt. Eng.*, **4631**, (2002).
14. R. G. Aviles, D. F. Muller, and P. L. Houston, "Quenching of laser-excited  $O_2(b)$  by carbon dioxide, water, and diatomic iodine," *Appl. Phys. Lett.* **37**, 358-60 (1980).
15. D. F. Muller, R. H. Young, P. L. Houston, "Direct observation of diatomic iodine collisional dissociation by  $O_2(b)$ ," *Appl. Phys. Lett.* **38**, 404-6 (1981)
16. R. F. Heidner, III, C. E. Gardner, G. I. Segal, and T. M. El-Sayed. "Chain-reaction mechanism for molecular iodine dissociation in the  $O_2(a)$ -iodine atom laser," *J. Phys. Chem.* **87**, 2348-60 (1983).
17. G. E. Hall, W. J. Marinelli, and P. L. Houston, "Electronic-to-vibrational energy transfer from excited atomic iodine ( $I^*(5^2P_{1/2})$ ) to molecular iodine ( $25 < v < 43$ )," *J. Phys. Chem.* **87**, 2153-61 (1983).

18. M. H. Van Benthem and S. J. Davis, "Detection of vibrationally excited molecular iodine in the dissociation region of chemical oxygen-iodine lasers," *J. Phys. Chem.* **90**, 902-5 (1986).
19. D. David, V. Joly, and Fausse, "High vibrational levels of iodine as intermediate states in the iodine dissociation by  $O_2(a)$ ," *Proceedings of the 7th International Symposium on Gas Flow and Chemical Lasers*, 1987.
20. H. V. Lilenfeld, "Oxygen-Iodine Laser Kinetics", Air Force Weapons Laboratory Technical Report AFWL-TR-83-1, 1983.
21. W. G. Lawrence, T. A. Van Marter, M. L. Nowlin and M. C. Heaven, "Energy transfer processes for  $I_2(X)$  of relevance to COIL," *Proc. SPIE-Int. Soc. Opt. Eng.* **2702** (Gas and Chemical Lasers), 214-225 (1996).
22. M. L. Nowlin and M. C. Heaven, "Collisional relaxation of highly excited vibrational levels of  $I_2(X)$ ," *J. Phys. IV 4* (C4, LASER M2P), C4/729-C4/737 (1994).
23. M. L. Nowlin and M. C. Heaven, "Energy transfer rate constants for highly excited rovibrational levels of molecular iodine," *J. Chem. Phys.* **99**, 5654-60 (1993).
24. W. G. Lawrence, T. A. Van Marter, M. L. Nowlin and M. C. Heaven, "Inelastic collision dynamics of vibrationally excited  $I_2(X)$ " *J. Chem. Phys.* **106**, 127-141 (1997).
25. J. S. Paschkewitz and M. C. Heaven, "COIL chemical kinetics package revisited: a re-analysis of molecular iodine dissociation rate data," *Proc. SPIE-Int. Soc. Opt. Eng.* **3931** (Gas, Chemical, and Electrical Lasers and Intense Beam Control and Applications), 169-178 (2000).
26. D. Cerny, R. Bacis, A. J. Bouvier, S. Poulat, and A. Topouzkhanian. "The dissociation of molecular iodine by metastable oxygen-I. Populations of A 1u and B 0u+ iodine states through Fourier transform spectrometry analysis," *J. Quant. Spectrosc. Radiat. Transfer* **47**, 9-18 (1992).
27. M. Nota, A. J. Bouvier, R. Bacis, A. Bouvier, P. Crozet, S. Churassy and J. B. Koffend, "The dissociation of iodine by singlet molecular oxygen; role of the vibrational reservoir state A'(2u)" *J. Chem. Phys.* **91**, 1938-40 (1989).
28. B. Barnault, A. J. Bouvier, D. Pigache and R. Bacis, "Absolute measurements of the molecular iodine high vibrational levels in the oxygen-iodine reaction," *J. Phys. IV 1* (C7, Int. Conf. Laser M2P, 2nd, 1991), C7/647-C7/650.
29. A. J. Bouvier, R. Bacis, A. Bouvier, D. Cerny, S. Churassy, P. Crozet, and M. Nota., "The dissociation of molecular iodine by metastable oxygen. II. Populations of reservoir states through laser excitation spectra," *J. Quant. Spectrosc. Radiat. Transfer* **49**, 311-23 (1993).
30. J. Tellinghuisen and L. F. Phillips, "Kinetics of  $I_2$  following photolysis at 1930 Å: Temperature dependence of A'-state quenching," *J. Phys. Chem.* **90**, 5108 (1986).
31. A. V. Komissarov, V. Goncharov, and M. C. Heaven, "Chemical oxygen-iodine laser (COIL) kinetics and mechanisms," *Proc. SPIE-Int. Soc. Opt. Eng.* **4184** (XIII International Symposium on Gas Flow and Chemical Lasers and High-Power Laser Conference), 7-12 (2001).
32. B. D. Barmashenko, E. Bruins, D. Furman, V. Rybalkin, and S. Rosenwaks, "Modeling of the gain, temperature, and iodine dissociation fraction in a supersonic chemical oxygen-iodine laser," *Proc. SPIE-Int. Soc. Opt. Eng.*, **4631** 2002.
33. T. J. Madden, private communication.
34. V. N. Azyazov, V. D. Nikolaev, M. I. Svistun, and N. I. Ufimtsev. "Luminescence of the oxygen dimole at the output of a chemical singlet-oxygen generator," *Quantum Electron.* **29**, 767-771 (1999).
35. S. J. Davis, "History of COIL diagnostics," *Proc. SPIE-Int. Soc. Opt. Eng.*, **4631**, 2002.

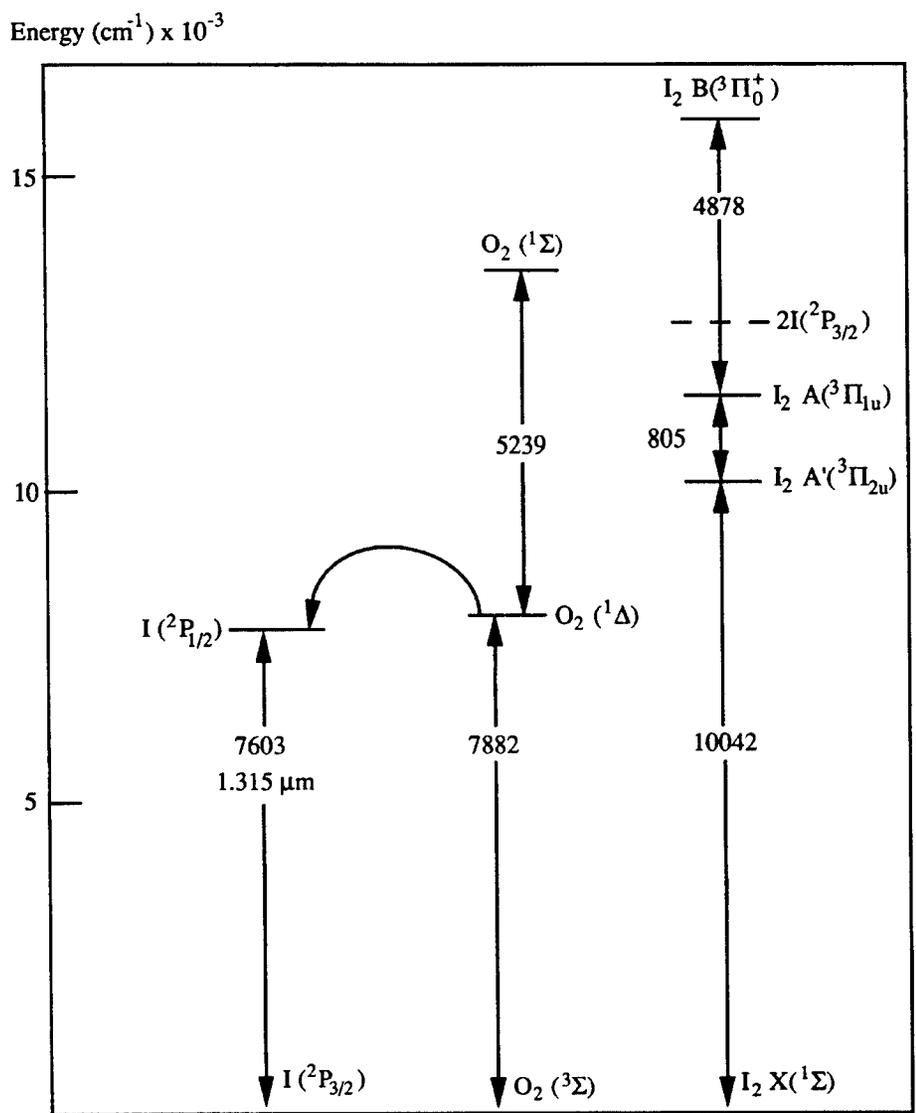


Figure 1. Energy level diagram showing the low-lying states of  $\text{O}_2$ ,  $\text{I}_2$ , and  $\text{I}$

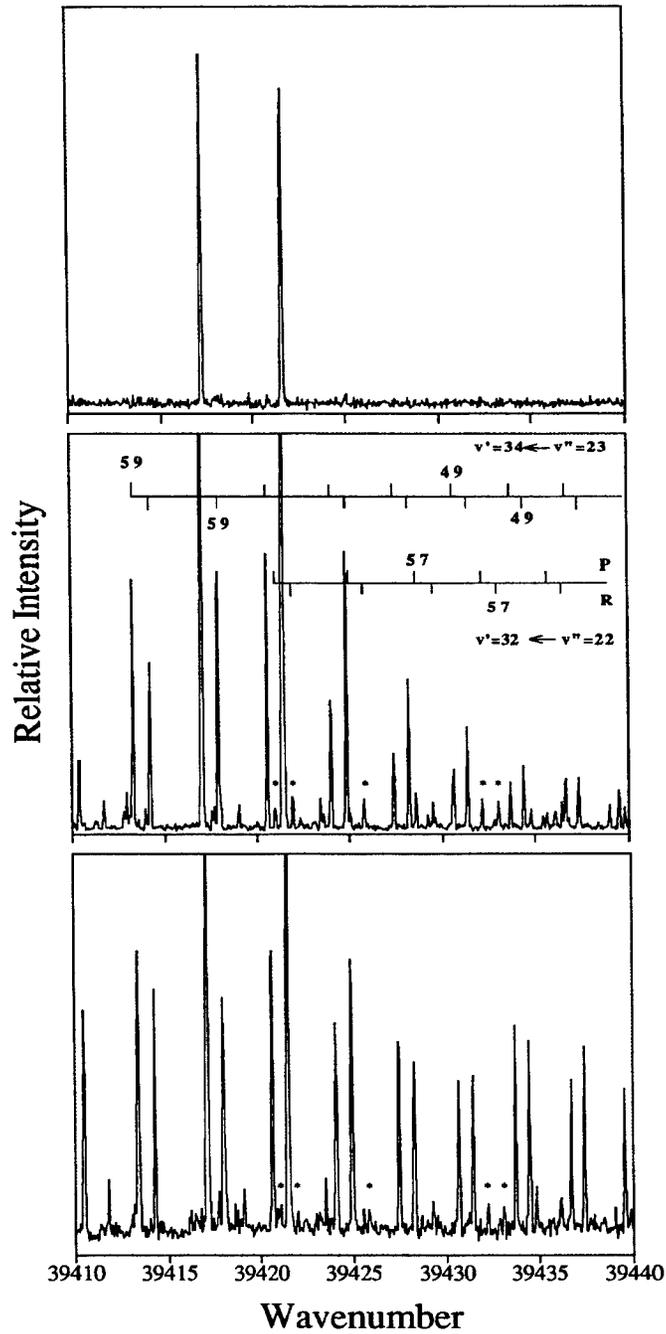


Figure 2. Spectra showing ro-vibrational level state preparation and collisional energy transfer. The upper trace demonstrates clean preparation of the  $I_2(X) v=23, J=57$  level under collision-free conditions. The middle and lower traces show the effects of ro-vibrational energy transfer induced by collisions with  $H_2O$  (middle trace) and Ar (lower trace). The peaks marked with asterisks originate from levels populated by vibrational energy transfer.

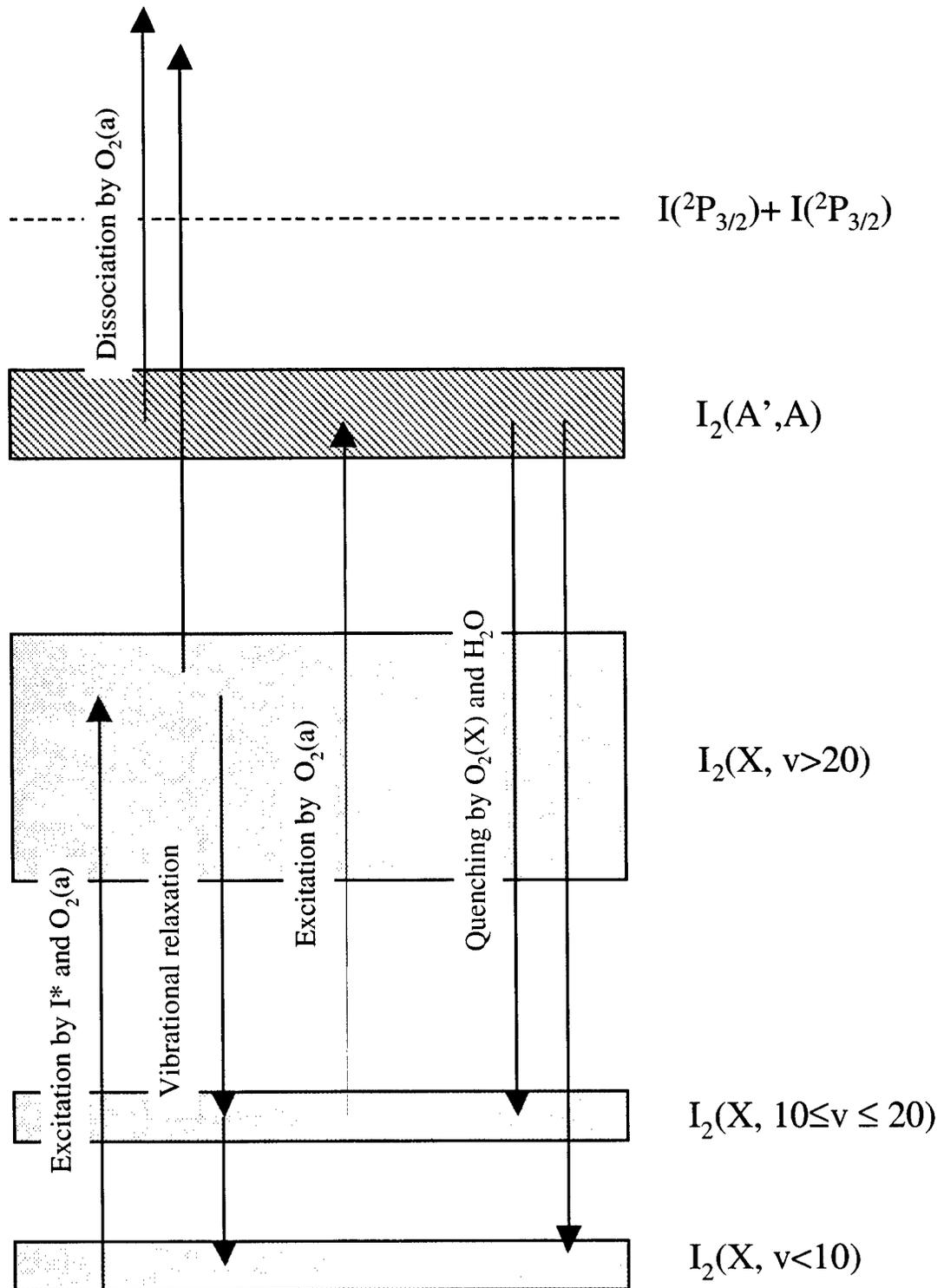


Figure 3. Schematic of the proposed dissociation mechanism proposed by Komissarov et al.<sup>31</sup>